VISCOSITY AND GELATION OF POLYMERS AND SOME PROPERTIES OF VAN DER WAALS LIQUIDS

BY

WILLIAM RICHARD KRIGBAUM

B.S., James Millikin University, 1944
M.S., University of Illinois, 1947

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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I. VISCOSITY OF BINARY POLYMERIC MIXTURES

Numerous attempts have been made to relate the viscosity of a binary polymeric mixture to the viscosities of the component polymers. Previous experimental investigations have been concerned with components differing only in molecular weight, or having repeating units quite similar in nature. Data is reported on three mixtures composed of components entirely dissimilar in nature, namely: rubber-polystyrene, rubber-ethyl cellulose, and ethyl cellulose-polyethylene glycol. Such mixtures might be expected to exhibit positive or negative deviations from ideal behavior.

From a consideration of the reduced viscosity of a single component in dilute solution

$$\frac{\eta_{sp}}{c} = [\eta] + bc \tag{1}$$

where

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right), \tag{2}$$

a relation for the specific viscosity of the mixture is obtained

$$\eta_{sp} = [\eta]_1 c_1 + [\eta]_2 c_2 + b_{11} c_1^2 + 2b_{12} c_1 c_2 + b_{22} c_2^2 \tag{3}$$

Here $[\eta]_1$ represents the interaction of a type one polymer segment and solvent, and b_{11} the interaction of two type one segments. The interaction of a type one with a type two segment is represented by b_{12}, which for an ideal mixture has the value

$$b_{12}^* = (b_{11} b_{22})^{\frac{1}{2}} \tag{4}$$

It has been pointed out (1),(2),(3) that coordination between the unethylated hydroxyl groups of ethyl cellulose in benzene results in clusters containing an average of two to three molecules. Addition of a polar compound such as water breaks these coordinate links and results in a lowered viscosity.

Since the addition of polyethylene glycol has precisely the same effect it was assumed that the quantities $[\eta]$ and b for ethyl cellulose decrease linearly with the weight fraction of polyethylene glycol (x_2) :

$$[\eta]_1' = [\eta]_1 - \rho_1 x_2 \tag{5}$$

$$b_{11}' = b_{11} - \omega_1 x_2 \tag{6}$$

Values of $[\eta]_i$ and b_{ii} were determined from the viscosity of each component by the method of least squares. Viscosity measurements on each mixture allowed calculation of an average value for b_{ij}; or in the case of the mixture ethyl cellulose-polyethylene glycol b_{12}, ρ_1, and ω_1. It was found that rubber-polystyrene exhibited a small positive deviation, rubber-ethyl cellulose a large negative deviation, and ethyl-cellulose-polyethylene glycol a large positive deviation. It appears, therefore, that the interaction constant b_{ij} gives some information concerning the interactions between dissimilar polymer molecules in dilute solution.

II. GELATIN OF POLYMERS

The existence of a gel is dependent upon the formation of extremely large, cross-linked molecules. The linear condensation polymer formed from glycol and a dibasic acid will be soluble regardless of how large the molecular weight becomes; however, the polymer formed from glycerol and a tribasic acid, in which a three-dimensional network can be built up, will ultimately form a gel. The formation of such a gel is not a continuous process resulting from the gradual growth of a network, instead the gel phase appears suddenly after a very definite extent of reaction has been reached. Appearance of the gel phase is independent of the temperature or presence of catalysts, and depends solely on the functionality of the reacting monomers.

From statistical considerations, the critical extent of reaction resulting in gelatin, p, has been derived by Flory (4) as

(7) $$p_c = 1/(f-1)$$

where f is the functionality of the monomer. If one reactant serves only to form branches p must be replaced by α, the probability that one branch unit will be connected to another.

The gelation of polyacrylic acid or a copolymer of maleic acid-styrene by barium hydroxide was followed by means of a Klett-Sommerson photoelectric colorimeter. It was found that the critical extents of reaction were considerably past the predicted points for both poly-acids in dilute solutions. In more concentrated solutions of polyacrylic acid partial gelation occurred at the expected point; however, not until the later point previously mentioned was the gelation complete. The theoretical treatment does not take into account the possibility of intramolecular cross-links. Although the measured extents of reaction were extrapolated to a fictitious zero volume, it is apparent that the effect of such intramolecular cross-linking was not entirely removed. This was not unexpected, since the functional groups along a chain are separated by small distances in the case of a polymeric reactant.

III. SOME PROPERTIES OF VAN DER WAALS LIQUIDS

A theoretical consideration of the volume (5) of a van der Waals liquid suggests some new rules, comparable to that of Trouton, relating coefficients of expansion and compressibility to heats of vaporization. According to the simplest and most reliable of these new relationships, the product of the coefficient of cubical expansion and the heat of vaporization, $\alpha\Delta H_v$, is the same for many liquids and equal to about 10 cal. deg. It is further shown that at a given temperature $\Delta H_v^2\beta/V$ is also constant where β is the compressibility and V the volume of the liquid. Certain corollary rules are derived by combining the above two with each other and with Trouton's law. These new rules should prove of some value in estimating compressibilities and heats of vaporization from coefficients of expansion.

BIBLIOGRAPHY

1. H. Suida, cellulosechemie, **12**, 310 (1931).
2. I. Okamura, cellulosechemie, **14**, 135 (1932).
3. H. Staudinger and F. Reinecke, Ann. **535**, 71 (1938).
4. P. J. Flory, J. Am. Chem. Soc., **58**, 1877 (1936).
5. F. T. Wall, J. Chem. Phys., **16**, 508 (1948).

VITA

The author was born September 29, 1922 near Beardstown, Illinois, the son of Daniel Dwight and Ella Mae Krigbaum. He attended primary and secondary schools in Decatur, Illinois, and was graduated from Decatur High School in 1940. In that year he enrolled in James Millikin University, from which he received his Bachelor of Science summa cum laude in 1944. From that time until 1946 he served in the Naval Reserve as a radar technician. He was married to Esther Jean Wolfe in Philadelphia, Pennsylvania, July 7, 1945. He entered the graduate school of the University of Illinois in June, 1946 as an American Chemical Society Fellow, receiving a Master of Science degree in chemistry in August, 1947.

He is a member of the American Chemical Society, Phi Lambda Upsilon, Pi Mu Epsilon, and Alpha Chi Sigma, and an associate member of Sigma Xi.

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